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Ambient Air Monitoring for Benzene 24-Hour Integrated Sampling in Six Cities

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24-Hour Integrated Sampling in Six Cities

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The improvement of benzene monitoring and analysis technology was an important secondary objective of this program. However, further research is needed to identify a more favorable collection medium than the Tenax that was used in this study.

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AMBIENT AIR MONITORING FOR BENZENE

24-HOUR INTEGRATED SAMPLING IN SIX CITIES

by

Barry E. Martin
Environmental Monitoring Branch

Thomas Clark
Quality Assurance Branch

Joseph Bumgarner
Analytical Chemistry Branch

Gary F. Evans
Analysis and Reports Branch

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has the responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Toxic Substances and the Office of Enforcement.

The declaration of benzene as a hazardous material provided the impetus for monitoring benzene in the atmosphere. Since benzene is one of the pollutants associated with internal combustion engines, monitoring sites for the present study were selected in metropolitan areas with high traffic density. Existing air quality monitoring sites were utilized to provide quick response. Since a method of monitoring benzene has not been standardized, the best available technology was employed. As deficiencies in the method became apparent, short-term research was applied to improve it quickly. Exact data were not obtained because high, variable concentrations of residual benzene on the adsorbent masked the sample concentrations. However, sufficient data were collected to assess the potential exposure of the population to benzene.

Thomas R. Hauser, Ph.D.
Director
Environmental Monitoring Systems
Laboratory
Research Triangle Park, N.C.

ABSTRACT

This monitoring program was initiated to assess the population exposure to ambient levels of benzene in conjunction with the announcement of benzene as a hazardous material. The program was conducted during the summer and fall of 1977.

Average benzene concentrations of 5, 18, and 19 $\mu g/m^3$, respectively, were measured in the widely separated cities of Dallas, Chicago, and Los Angeles. The precision of these data is estimated to be ±26 percent of the measured values.

The improvement of benzene monitoring and analysis technology was an important secondary objective of this program. However, further research is needed to identify a more favorable collection medium than the Tenax that was used in this study.

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SECTION 1

INTRODUCTION

As a result of the designation of benzene as a hazardous air pollutant under Section 112 of the Clean Air Act, monitoring data were required to assess general population exposures and to evaluate the population risk. Preliminary monitoring data were desired by the middle of August 1977.

Although a standard method for monitoring ambient benzene did not exist, data were to be collected immediately using the best available technique, rather than by developing a method through an experimental program. As problems became apparent, they were resolved by short-term research. Hence, the method described in Appendix A represents the most recent techniques used, but these were not necessarily throughout the benzene monitoring program.

In July 1977 the objective was to take ambient air samples for 10 days in six major metropolitan areas. Monitoring was extended into October 1977 for three cities, however, because the results of these early measurements indicated that improvements in the monitoring method were needed.

Monitoring was planned in metropolitan areas with high traffic densities because the major sources of benzene are automobile emissions and gasoline evaporation. Since CO is also an automotive pollutant, siting criteria already published for CO were useful in selecting the benzene monitoring sites.

Five sampling locations were chosen within each of the six cities: New York, St. Louis, Los Angeles, Dallas, Boston, and Chicago. A range of urban characteristics was represented by the sampling sites, including street canyon, peak neighborhood, corridor, urban and background area.

A quality control program was implemented to minimize the introduction of erroneous data. Due to the time restraints and nature of the study, the quality control program was somewhat limited, but it did include controls over benzene standards used for calibration, preparation of sampling cartridges, sampling, and analysis of samples.

To complete the monitoring program in the allocated time using the best available techniques, various tasks were assigned to several branches of the Environmental Monitoring Systems Laboratory (EMSL), as follows.

The Environmental Monitoring Branch (EMB) was required to visit cities and select sites; procure, calibrate, transport, and install sampling and support equipment; perform sampling; and implement a quality control program for sampling.

The Quality Assurance Branch (QAB) provided technical expertise in methods development and quality control procedures; provided approximately 50 quality control samples for random insertion among field samples; and performed sample liaison (receipt, logging, and distribution of quality control and field samples).

The Analytical Chemistry Branch (ACB)was assigned to prepare approximately 600 sampling cartridges (500 for field sampling and 100 for QAB work); develop analytical methodology; and analyze field and quality assurance samples. Much of the method development and analytical work was actually performed under contract by the Research Triangle Institute (RTI).

The Statistical and Technical Analysis Branch (STAB) statistically analyzed the data; assisted with the design of sampling and quality control procedures; and coordinated the preparation of a final project report.

SECTION 2

SUMMARY AND CONCLUSIONS

The average ambient concentrations of benzene in Dallas, Chicago, and Los Angeles were estimated at 5, 18, and 19 $\mu g/m^3$, respectively. The positive bias associated with the observed values is estimated at 44 percent of the true value as determined by control samples. The coefficient of variation for an individual analysis made by the ambient benzene measurement method was approximately 26 percent.

The major reason for the considerable measurement error in the analyses was the large and variable concentration of residual benzene in the Tenax used for sample adsorption. Removal of impurities from the Tenax polymer resin was difficult and time consuming, but after cleanliness was apparently achieved (as verified by analysis), benzene was likely to reappear for at least two reasons: (1) the Tenax was most probably contaminated with benzene during the manufacturing process, and its presence was detected later due to diffusion to the surface; (2) the polymer resin material might alter to benzene as a result of chemical reaction.

The benzene monitoring program contributed to improvements in the system design used to desorb the collected benzene from the Tenax and to the development of a system to consistently and accurately prepare quality control samples.

Before a benzene measurement method used can be standardized, further research is needed to find a better adsorbent material for benzene and to develop a sampling cartridge that can be reliably sealed and conveniently used. The adsorbent material should offer a consistently low benzene background, and not react chemically with benzene or other compounds to form benzene.

SECTION 3

EXPERIMENTAL METHOD

The sample collection and analysis techniques used in the study are presented in this section. Short-term research that was conducted to validate a technique or to resolve a specific problem is also discussed.

SAMPLE COLLECTION

Benzene was adsorbed onto Tenax resin beads packed in a sampling cartridge. The cartridge was prepared from a cleaned stainless steel tube of 7.9 mm inside diameter (i.d.) and 300 mm length. The Tenax was cleaned and packed in the center section (250 mm) of the tube, and a glass wool plug (25 mm length) was placed in each end to hold the Tenax in position. Both ends were sealed with compression fittings to complete the assembly of a sample cartridge. In field use, the fittings were removed and one end was connected to an ambient air sampler for the collection of a 24-hour benzene sample. After sampling, the compression fittings were reinstalled and the cartridges sent to the analysis laboratory.

Details of the sampling procedure are presented in Appendix A. As the appendix indicates, the samples were refrigerated at -18°C (except during sampling) to reduce the diffusion of benzene from the Tenax.

In support of the monitoring study, research was conducted to assess the diffusion of benzene in Tenax resin, to determine the maximum sampling rate without benzene breakthrough, to verify the uniformity of quality control samples, and to assess the adequacy of the cartridge sealing procedure. This research is described below.

Benzene Diffusion in Tenax

One of the prepared, unexposed sampling cartridges was first analyzed for benzene, then stored at room temperature for 3 days, and later analyzed twice in successive runs on the same day. The sample cartridge again was stored at -18°C for 3 days and analyzed, then stored 1 day at -18°C and analyzed, and finally stored another 13 days at -18°C and analyzed. After the original analysis, the Tenax was exposed to hydrocarbon-free (HCF) air in an attempt to cleanse the benzene from the resin, but subsequent analyses revealed that this exposure did not affect the quantity of benzene measured later. Table 1 summarizes the above procedure and the results of the analysis.

An unexpected result occurred in the second run on the second day of analysis (10/21/77): no measurable benzene was detected in the Tenax resin in which residual benzene had just been measured. A possible explanation for this effect is that benzene, which apparently was dispersed throughout the Tenax resin, had been desorbed from the surface of the Tenax beads during the day's first analysis, but was not replaced by benzene diffusing from the interior of the beads before the second analysis. Consequently, no benzene was measured during the second analysis.

Whether diffusion occurs only at elevated temperatures (20°C and above) is unknown. Therefore the sample was stored at -18°C for 3 days and analyzed. Since a relatively high benzene concentration was found, the cartridge was refrigerated for a shorter period of time to assess the effects of time. In this case, a significantly lesser quantity of benzene was measured, so the sample was refrigerated for a substantially longer period (13 days). The concentration found from this time period was approximately the same as that of the 3-day storage, which indicates a maximum value is attained within about 3 days. The overall results, however, are somewhat inconsistent because higher benzene concentrations were recorded after 3 days of refrigerated storage than had been measured at room temperature.

TABLE 1. RESIDUAL BENZENE IN UNEXPOSED TENAX FROM SAMPLE CARTRIDGE (NO. 1053)

Date	Tenax Conditions	Benzene (ng)
10/18/77	Blank as received from EPA	39.2
10/21/77	HCF air loaded. Tube had been stored for 3 days at room temperature	39.0
10/21/77	Analyzed immediately after previous run (no connections were broken)	0.0
10/24/77	Storage at -18°C since previous run	79.0
10/25/77	Storage at -18°C since previous run	35.0
11/8/77	Storage at -18°C since previous run	85.0

Sampling Rate

A prime consideration in selecting the appropriate sampling rate for Tenax was ensuring the availability of sufficient pollutant quantity for good analytical resolution, without losing any of the sample (i.e., without breakthrough occurring). To detect breakthrough, two cartridges were placed in series. Analysis of the second (downstream) cartridge indicated whether or not breakthrough in the first (upstream) cartridge had occurred.

In many experiments with various sampling flow rates, breakthrough generally occurred after 17 liter of ambient air had passed through 2.2 g of Tenax. For the present monitoring study, a safety factor of approximately 2.5 seemed advisable, so the total sampling volume was set at approximately 7 liter. During the 24-hour sampling a flow rate of 5 cm^3/min was maintained.

Quality Control Samples

Quality control samples were prepared with known concentrations of benzene adsorbed on Tenax. To generate the benzene, a permeation tube with nitrogen carrier gas was pulled through a sample cartridge, as indicated in Figure 1. At the beginning of the program, six quality control sample cartridges were prepared simultaneously using a manifold. The total flow rate was measured and was assumed to be uniformly distributed among the cartridges. However, analyses of some of these cartridges later revealed nonuniform concentrations. Presumably the Tenax was packed nonuniformly in the six tubes, resulting in a variable pressure loss and flow rate through the cartridges. After the nonuniformity was determined and rectified by individual preparation of samples, good comparisons among cartridges were attained.

SAMPLE ANALYSIS

To analyze a sample, benzene was measured by (1) recovery with heat desorption, (2) cryogenic trapping on silanized glass beads in liquid nitrogen, (3) separation in a specially prepared column, and (4) analysis with a flame ionization detector (FID). Specifications of the apparatus and of the operating conditions are presented in Appendix A.

Each sample was desorbed at a temperature of 250°C for 10 minutes utilizing a 400-W heater. Developmental work was required in order to distribute the heat uniformly over the exterior surface of the sample, and to raise the sample temperature rapidly. The samples were rapidly placed in the heater and connected to the sample recovery apparatus while the heater was operating. Heat was generated by two diametrically opposed coils placed along the length of the cartridge. An aluminum enclosure both reduced heat loss and, through high thermal conductivity, assisted with circumferential heat distribution. Rollers on the heater assembly and quick-connect fasteners on the sample cartridge assisted with attaching the hot assembly to the sample recovery tubing.

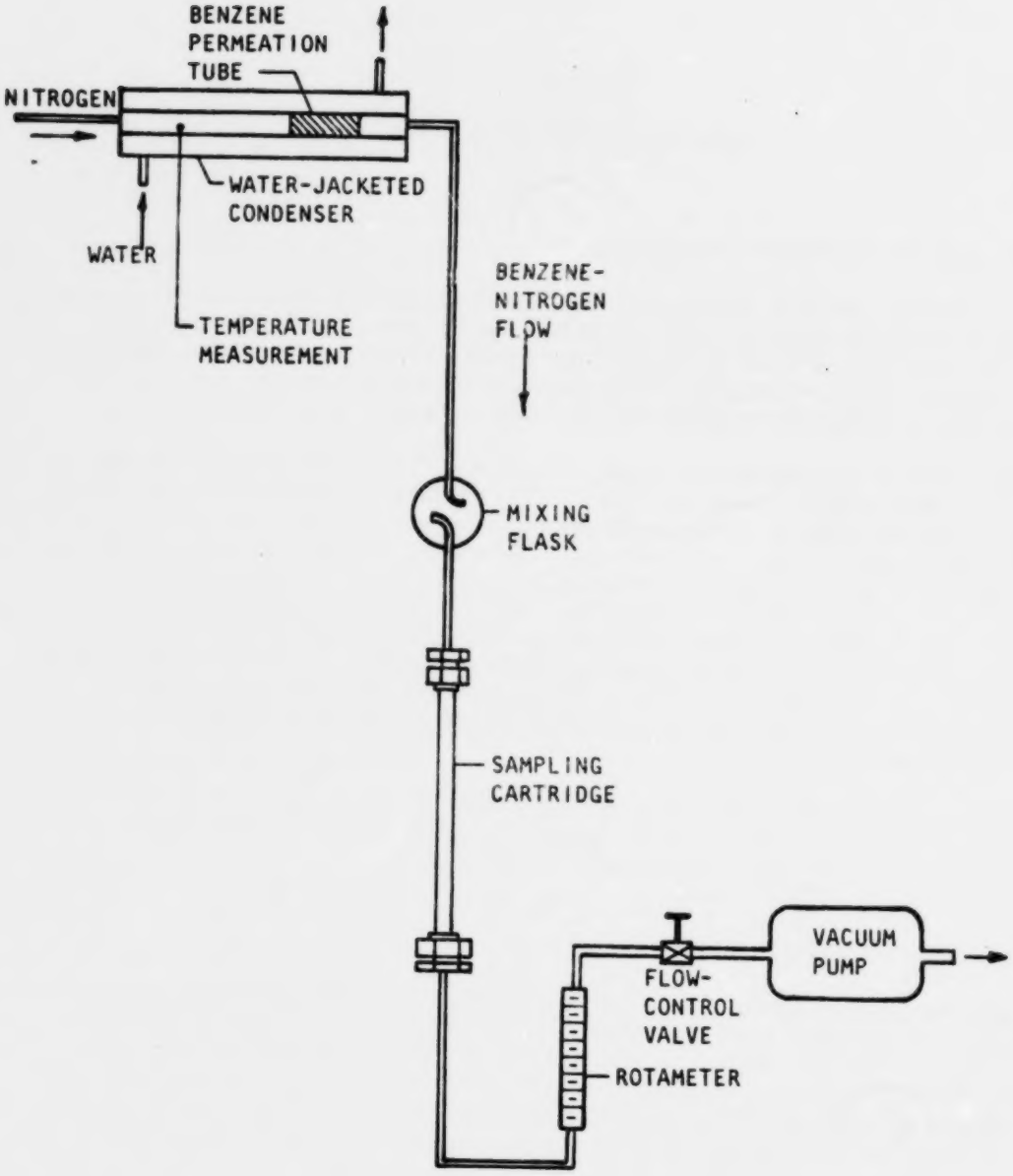

Figure 1. Benzene generating system.

SECTION 4

QUALITY CONTROL PROCEDURES

EXTERNAL QUALITY ASSURANCE PROCEDURES

An external quality assurance plan was initiated by QAB/EMSL to supplement the quality control procedures developed by the contractor for this study, for the analysis of the collected field samples. This plan assisted in determining the performance of analysis procedures used by the contractor, and provided a method of qualifying the sample data.

The external controls consisted of randomly inserting among each day's collected field samples both unexposed (blank) sample cartridges and exposed samples of known benzene concentrations. These quality control samples were analyzed as if they were field samples; moreover, because of uncertainties in the analysis procedures for benzene, a large number of these samples was utilized with respect to field samples. Two blank cartridges and two prepared samples were included with every four field samples undergoing analysis. This large ratio of quality control samples to field samples was dictated by the high and variable blank sample values that were obtained using the Tenax material, and the limitation of being able to perform only one analysis per field sample.

Field sample cartridges were stored under refrigeration until they were analyzed by the contractor. Both the blank and benzene-exposed control samples were then randomly introduced to the sample set.

EXTERNAL QUALITY ASSURANCE SAMPLES

Benzene concentrations from 50 to 1000 ng per cartridge were necessary to provide an adequate quality control check of the contractor's analysis procedure. To obtain these concentrations, nitrogen was passed over the benzene permeation tube, through the sample cartridge; the gas was measured by a rotameter and controlled with a flow control valve (see Figure 1). A constant flow rate of 57 cm^3/min ±2 percent was maintained through the sample cartridge.

The weight loss of the benzene permeation tube was determined gravimetrically and a QC analysis confirmed that benzene was the only compound permeated. Sample concentration was calculated from the gravimetric permeation rate. The obtained value was validated independently by three laboratories within Research Triangle Park (RTP), NC, using gas chromatographs (GCs) with FIDs.

Quality control samples were prepared each analysis day and were presented to the contractor as part of a complete sample set, which consisted of four field samples, two blank samples, and two benzene-exposed quality control samples. Routinely, one quality control sample containing approximately 100 ng benzene, and one containing approximately 50 ng benzene, were sent with the sample set. Periodically, samples with benzene concentrations as high as 800 ng per cartridge were included.

EXTERNAL QUALITY ASSURANCE VERIFICATION FOR BENZENE

Since standard calibration gases were not available in the concentration range of interest (0-10 ppm), the concentrations provided by the permeation tube used to prepare the quality control samples were verified by three RTP laboratories. At the beginning of the study, the samples were prepared with HCF air as a diluent. But concentrations determined by analysis and by weight loss calculations of the permeation tube using this diluent did not agree within 20 percent. The discrepancy was traced to hydrocarbon impurities in the permeation tube, as detected by the GC.

For those quality control samples prepared with HCF air, the average of the three analysis values from the RTP laboratories was used in the study. In subsequently prepared quality control samples, nitrogen was used as the dilution gas, and benzene permeation tubes were used that were known to be free of hydrocarbons. As presented later in the quality control results, strong agreement was obtained between the permeation rate of the tubes and GC analyses for the second set of quality control samples.

Toward the end of the monitoring study, a more convenient and equally accurate method was used to prepare the quality control samples. Cylinders containing 10 ppm benzene in nitrogen were purchased. This gas mixture was further diluted with nitrogen and pulled through the sample cartridges. The calculated sample concentration from the benzene cylinder agreed with GC analyses of sample cartridges.

INTERNAL QUALITY CONTROL PROCEDURES

An in-house quality control program was performed in order to insure the proper operation of the analytical system. The program consisted of having the contractor load known concentrations of benzene onto Tenax in blank cartridges (supplied by EPA) and then analyzing these cartridges as if they were field samples. Blank cartridges were also analyzed. Clean air and nitrogen used in the preparation of quality control samples were intermittenly analyzed throughout the program to ensure no benzene contamination.

INTERNAL QUALITY CONTROL SAMPLES

To evaluate the performance of the analytical system, sample cartridges were spiked with benzene by the contractor. As mentioned previously, an air dilution system was one of two methods used to produce quality control samples.

This system is illustrated in Figure 2 and consists of two stages of mixing, both of which received approximately equal injections of HCF air. The flow from a 9.27 ppm benzene cylinder was diluted with HCF air so that the concentration entering a cartridge was 0.04 ppm. The time of exposure determined the total weight of benzene collected on the Tenax. Typically, this weight was 125 ng per cartridge, which is a concentration of 125 $\mu g/m^3$.

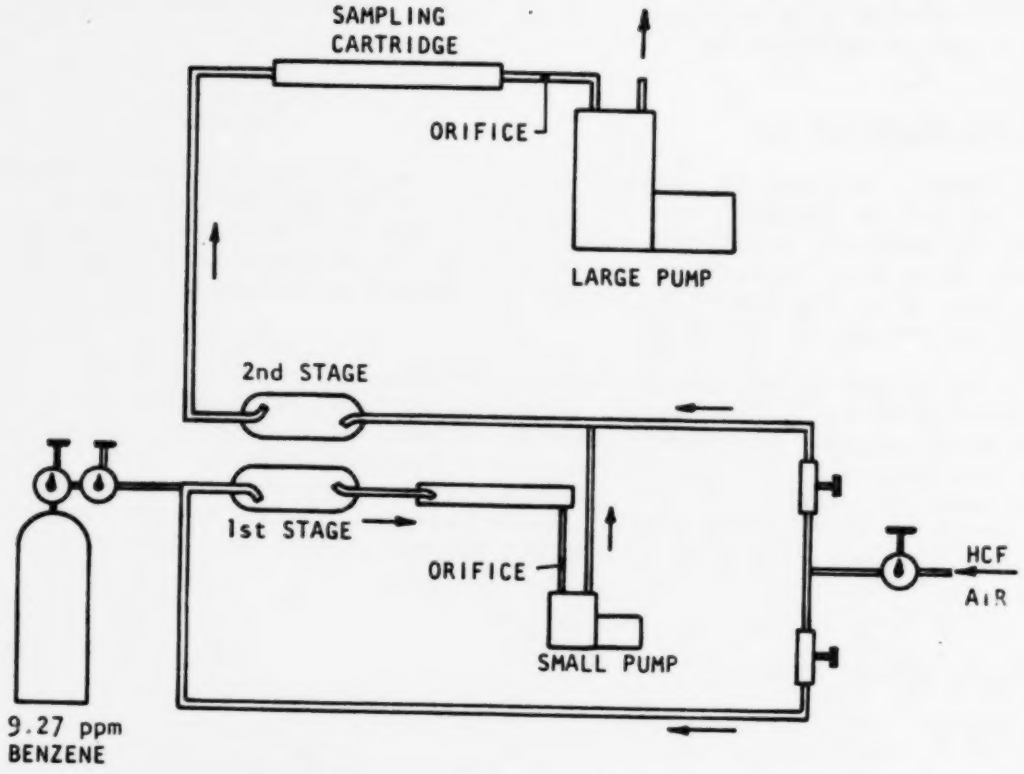

Figure 2. Two-stage benzene dilution system.

SECTION 5

STUDY RESULTS

The monitoring study produced a set of values for ambient benzene concentrations obtained from sampling sites within each of three cities. Quality control data were used to estimate the accuracy and precision of these concentration values.

BENZENE CONCENTRATIONS

Table 2 presents the ambient benzene concentrations observed in Chicago, Dallas, and Los Angeles. The average values in Chicago and Los Angeles were approximately equal, but that in Dallas was only about one-fourth as high. Each value in Table 2 was obtained by subtracting 9 $\mu g/m^3$ from the measured value (the constant 9 is the average correction determined for the residual benzene in the Tenax).

The amount of residual benzene in the Tenax was equal to a large percentage of the ambient level. Also, the residual value varied among unexposed samples. The average quantity of benzene in unexposed (blank) quality control samples was 48.2 ng with a standard deviation of 30.7 ng. The lower and upper 95 percent confidence limits were 36.1 and 60.4 ng, respectively, which translates to concentrations of 7 and 11 $\mu g/m^3$ benzene. Hence, the average value of 9 $\mu g/m^3$ was subtracted from each data point, as stated.

QUALITY CONTROL RESULTS

Accuracy

The accuracy of the analysis procedure was determined from quality control samples spiked with known quantities of benzene. Quality control data were expressed as precentages of concentration differences, defined as follows:

$$C_d = 100(C_a - C_s)/C_s \qquad (1)$$

where C_d = concentration difference between analyzed and spiked values, percent

C_a = analyzed value of prepared quality control sample, $\mu g/m^3$

C_s = concentration determined at the time that a quality control sample was spiked, $\mu g/m^3$.

The value of C_d, which is the bias estimate for individual field samples, is +44 percent.

Precision

Precision was evaluated using replicate analyses of samples prepared by the contractor. The coefficient of variation for a single analysis was 26 percent. The value of this coefficient did not appear to vary as a function of benzene concentration, but wide scatter in the data precluded regression analysis of precision as a function of concentration.

TABLE 2. AMBIENT BENZENE CONCENTRATIONS IN CHICAGO, DALLAS, AND LOS ANGELES DURING SUMMER AND AUTUMN OF 1977 ($\mu g/m^3$)

	Chicago	Dallas	Los Angeles
	26	4	14
	23	4	11
	13	4	26
	9	8	12
	8	6	15
	9	4	23
	14	4	18
	30	5	20
	7	1	20
	14	1	13
	12	0	17
	12	11	27
	22	3	24
	11	3	17
	43	0	18
	29	5	19
	26	2	23
	20	22	30
	22		
	27		
	7		
	9		
	11		
Average	18	5	19

SECTION 6

PROBLEMS AND RECOMMENDATIONS

Because of the urgent need for ambient benzene data at the time of this study, the full development of satisfactory sampling and analytical techniques was not possible prior to commencement of the monitoring effort. Thus, as technical problems arose, short-term methods research was performed in conjunction with the ongoing monitoring program.

Research activities addressed the extent and effects of residual benzene in the adsorbent material (Tenax) and the development of sampling and analytical equipment.

The major problems encountered with the use of Tenax as an adsorbent were that (1) the residual benzene concentration in the Tenax was large compared to that of a field sample, (2) this concentration was highly variable, and (3) it could not be completely removed from the Tenax. Since these effects are believed to be related to the stability and reactivity of the material, materials other than Tenax should be considered in future benzene monitoring programs unless a routine procedure can be developed to satisfactorily clean the Tenax prior to field exposure. Either an alternative material or an alternative collection method should be sought. Furthermore, the material sought should be compatible with solvent desorption of benzene rather than thermal desorption, for the following reasons:

1. With thermal desorption, only one analytical result can be obtained for each sample, thus precluding developmental methods comparisons, analytical accuracy evaluations or replicate statistical analyses for precision.

2. The extensive tubing lines, fittings, and valves used with thermal desorption provide opportunities for leaks.

3. External standards must be used for calibration with thermal desorption, due to the inherent nature of the method, while internal standards such as those used with solvent desorption are more accurate.

4. Solvent desorption is less costly, less labor intensive, and less time consuming.

5. With thermal desorption, constant and reproducible temperatures and gas flow rates are difficult to maintain.

Future research is needed to develop a solvent desorption method, assuming that an adsorption method is used to collect the sample.

Leakage was also a problem with the sample cartridges. When the caps were tightened sufficiently to prevent it, the cartridge tubes became so bulged that subsequent removal of the caps was difficult. After the samples were collected, some of the tubes required grinding before they could be resealed. Alternative apparatus should be developed to collect samples.

APPENDIX A

A METHOD OF DETERMINING BENZENE IN THE ATMOSPHERE

The method described evolved during the benzene monitoring program. As apparatus and procedures were improved, the changes were incorporated in subsequent analyses. Areas that were investigated were the desorption heater design, the preparation of uniform quality control samples, sealing of the sampling cartridges, and the temperature effect on the diffusion of benzene in Tenax resin.

PRINCIPLE

Benzene was adsorbed from ambient air onto Tenax polymer resin. Subsequently the benzene was desorbed by heating the resin, and, through use of a carrier gas (helium), the concentration was measured chromatographically with a dual FID.

APPLICATION

The method described is applicable to the measurement of benzene in ambient air using a 24-hour sampling period. CAUTION: Benzene is a hazardous air pollutant and care must be exercised to protect operators from breathing its fumes.

SENSITIVITY AND RANGE

The limit of detection is approximately 0.1 $\mu g/m^3$, and the maximum of the range is 32,000 $\mu g/m^3$. The range can be increased by extending the calibration range or by diluting samples in which the concentration exceeds the maximum limit.

PRECISION

The relative standard deviation of replicate gas chromatographic analyses of standard gas mixtures is within 26 percent.

ACCURACY

The accuracy is approximately 44 percent.

APPARATUS

The apparatus used during sampling, sample recovery, and sample analysis are described below and illustrated in Figures A-1 through A-4.

Apparatus for Sampling

Sampling cartridge - Tenax in 9.5 mm (0.375 in) outside diameter (o.d.) by 7.9 mm (0.313 in) inside diameter (i.d.) by 300 mm (12 in) long 316 stainless steel tubes, glass wool plug on each end of Tenax, tube sealed with Swagelok compression fitting on each end (Figure A-1).

Sampler - with auxiliary equipment, including:

- Pump - capable of maintaining a minimum pressure ratio of 0.53 across the critical-flow orifice at a flow rate of 5 cm^3/min
- Critical-flow orifice (Lodge, et al, 1966) - capillary used to control air flow rate at 5 cm^3/min
- Air-flow meter - bubblemeter used for calibrating critical-flow orifice;
- Indicating silica gel - to detect excess moisture flowing between flowmeter and sample cartridge
- Timers - 7-day and elapsed time to measure interval between runs and time of sampling
- Air filters - to provide clean air through critical-flow orifice to prevent plugging and erroneous flow rate
- Tubing - miscellaneous lengths of 316 stainless steel tubing, connectors, and tees to adapt the sampler for single, duplicate, or tandem sampling
- Bags - plastic, for shipping and storing sample cartridges when not in use (Ziploc)
- Barometer - for measuring atmospheric pressure
- Thermometer - for measuring ambient air temperature
- Hygrometer - for measuring relative humidity of ambient air
- Freezer - capable of -18°C operation for storing samples

Apparatus for Sample Recovery

Desorption heater - 400-W, with temperature controller, designed to heat a sample cartridge to 250°C in 10 minutes
Needle valve - 1.588 mm (0.0625 in) diameter, 316 stainless steel
Four-port valve - 1.5888 mm (0.0625 in) diameter, 316 stainless steel, high temperature (150°C) type (Valco)
Tubing - various lengths of 1.588 mm (0.0625 in) o.d. by 1.016 mm (0.040 in) i.d., stainless steel tubing

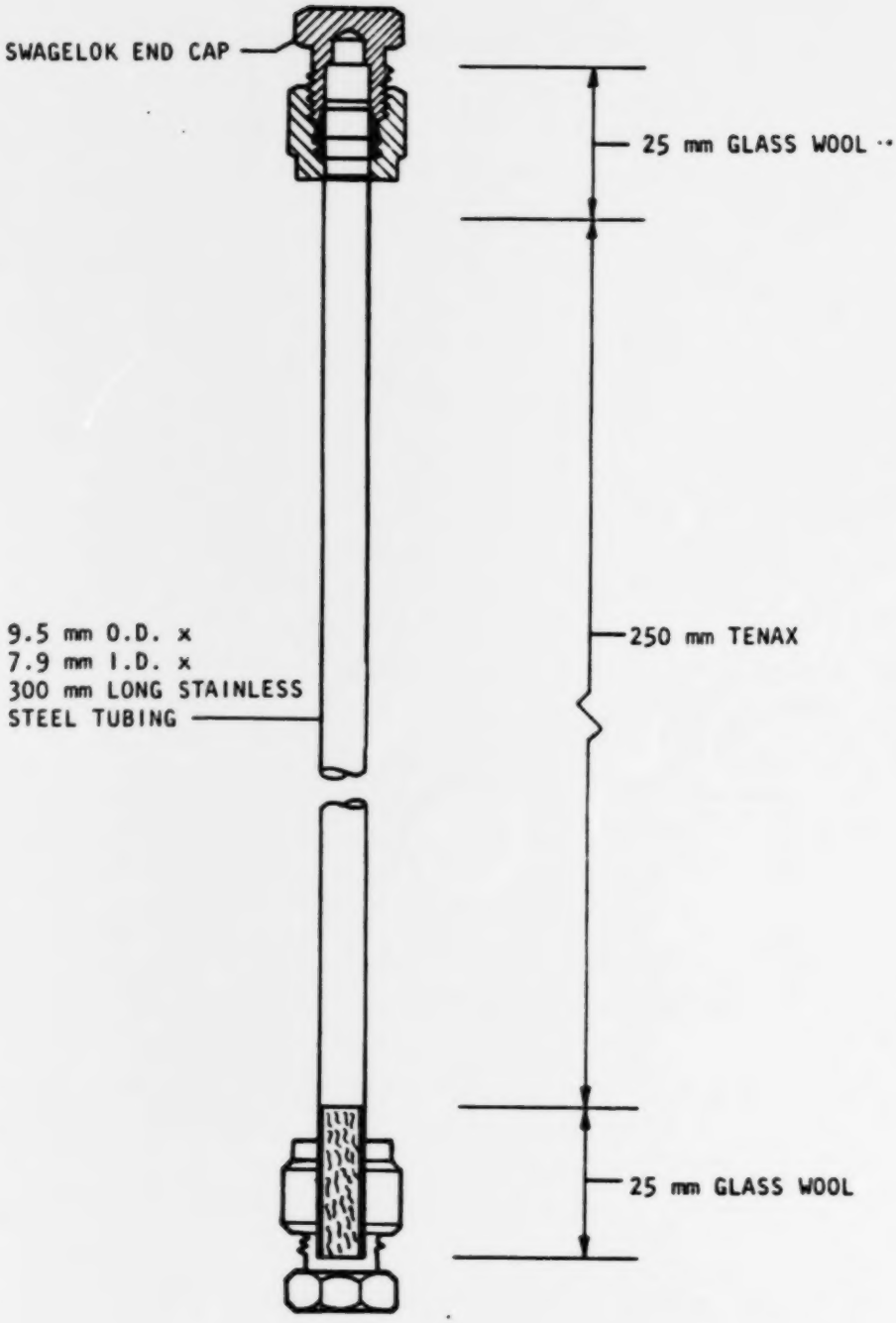

Figure A-1. Sampling cartridge.

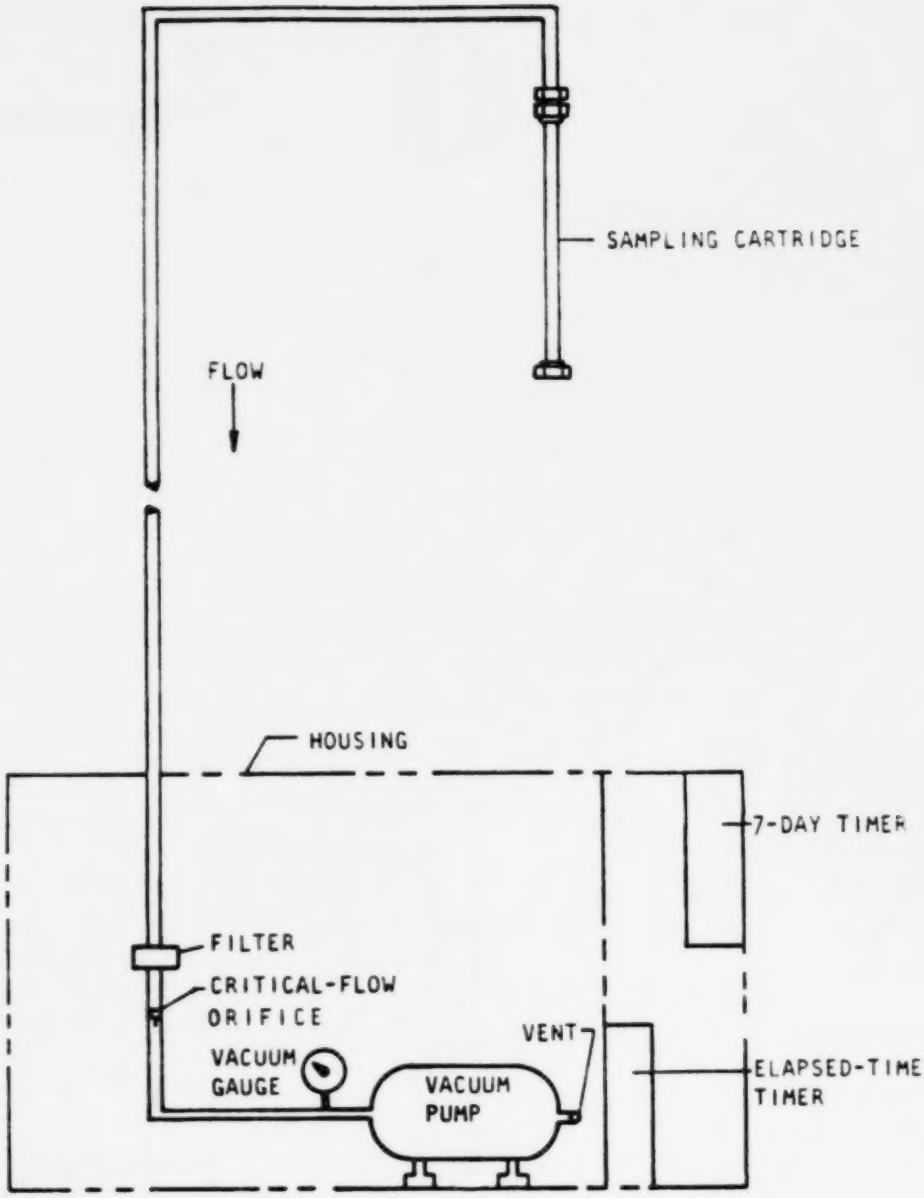

Figure A-2. Single sampler for benzene.

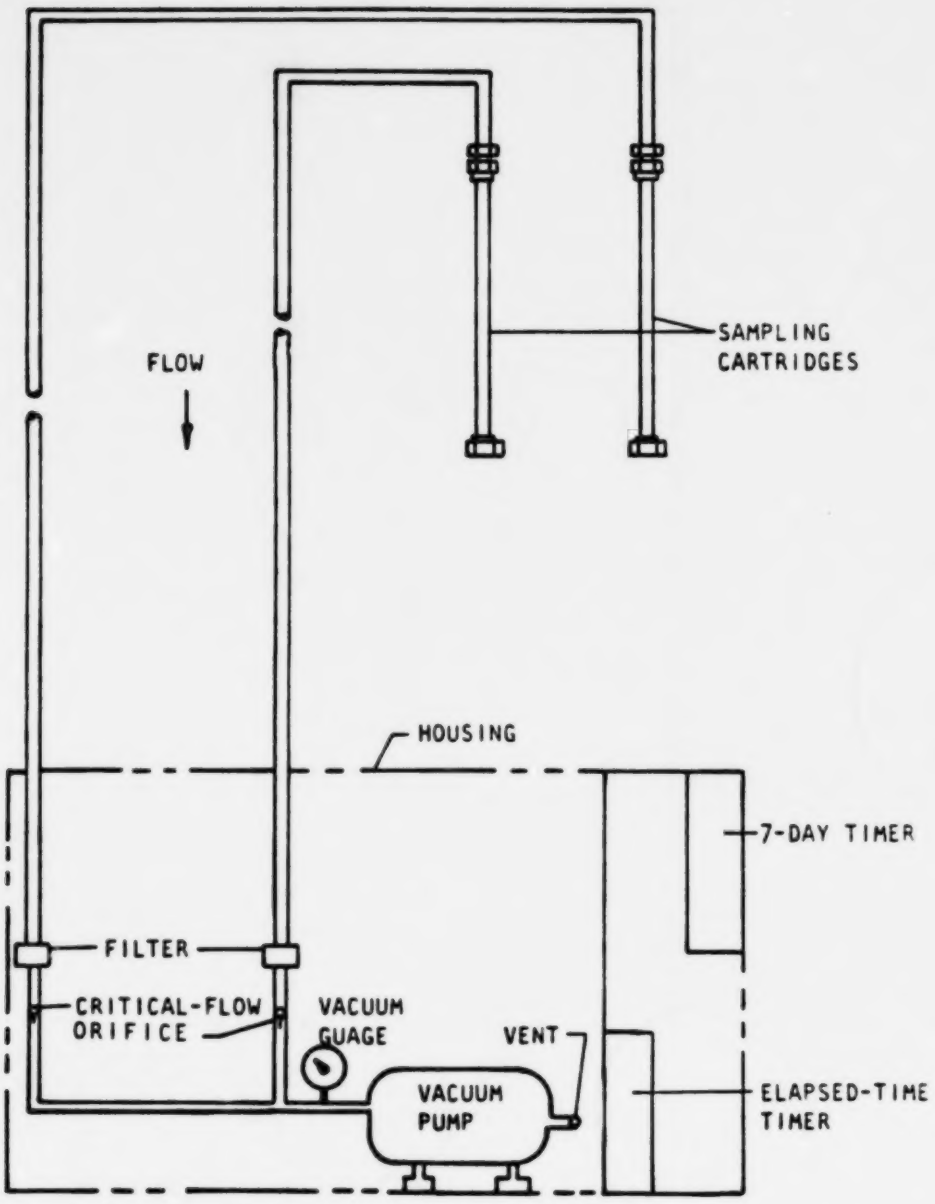

Figure A-3. Duplicate sampler for benzene.

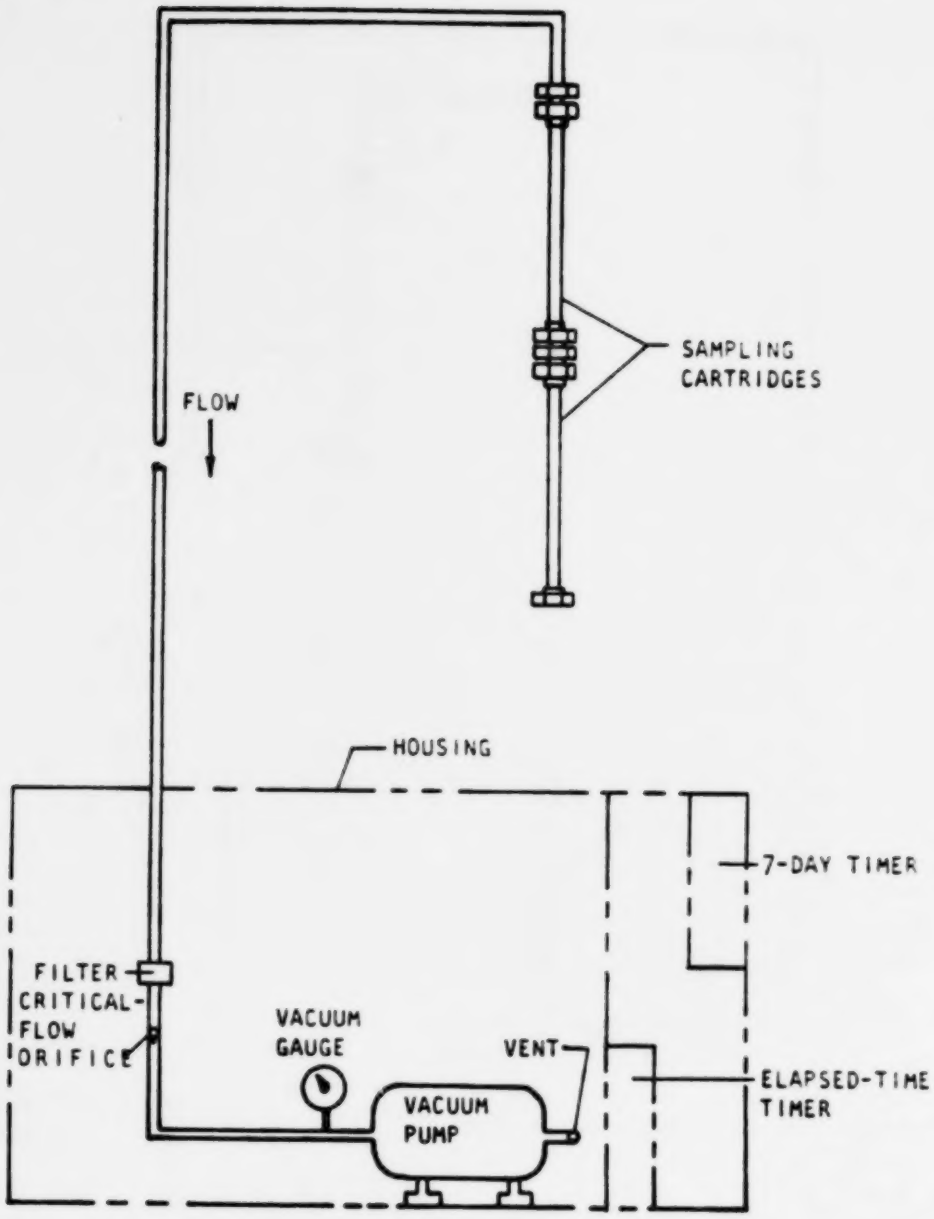

Figure A-4. Tandem sampler for benzene.

Apparatus for Sample Analysis

Gas chromatograph - with dual flame ionization detector (Perkin-Elmer 3920) and with strip chart recorder (Linear, Model 385)
Data acquisition system - Hewlett-Packard model 3352, for analyzing the output of GC and determining the benzene concentration
Six-port valve - 1.5888 mm (0.065 in) diameter, 316 stainless steel, high temperature (150°C) type (Valco)
Tubing - various lengths of 1.5888 mm (0.0625 in) o.d. by 1.016 mm (0.040 in) i.d. nickel tubing
Miscellaneous fittings - Swagelok compression fittings; quick connect fasteners; and minimum-internal-volume unions of same nominal diameter and type of material as the tubing
Chromatographic column - 0.5 mm (0.02 in) i.d. by 61 m (200 ft) stainless steel tubing, MBMA m-bis with a stationary phase of (m-pheno-xyphenoxy) benzene plus Apiezon L support-coated open tubular (SCOT), supplied with temperature controller-programmer (Perkin-Elmer)
Trap - 1.588 mm (0.0625 in) o.d. by 1.016 mm (0.040 in) i.d. by 300 mm long nickel tubing packed with 60/80 mesh silanized glass beads (Liquid nitrogen surrounded the tubing during trapping. Oil at 190°C was used to vaporize benzene from the trap.)
Flow controller - capacity to 10 cm^3/min (6 cm^3/min used)
Flow meter - 6 cm^3/min midrange capacity
Gas sampling loop - 1.1 m , gravimetrically calibrated, for cross-checking benzene standards used to calibrate the GC

REAGENTS

All reagents used in this porcedure should be of a chromatographic grade that conforms to the specifications established by the Committee of Analytical Reagents, American Chemical Society. For a chemical not covered by these specifications, the best available grade should be used.

The following is a summary of the reagents used during sampling and sample analysis.

Reagents for Sampling

Tenax - polymer resin adsorber for benzene
Glass wool - borosilicate
Silica gel - moisture indicator in flow meter during sampling

Reagents for Sample Analysis

Helium - zero-grade gas, for chromatographic carrier gas
Combustion air - containing less than 1.3 mg/m^3 hydrocarbons (2 ppm methane), for operating FID Benzene calibration standards - purchased
Benzene calibration standards - purchased cylinders (Scott Environmental Research) containing 13, 72, and 350 ppm benzene (The first two cylinders were used directly. The latter was used to prepare 2, 5, 41, and 200 ppm standards.)

PROCEDURES

The following procedures were employed during sampling, and sample recovery and analysis.

Sampling Procedure

The sampling procedure involved preparation of the sample cartridges, special handling precautions, and sample collection procedures.

Sample Cartridge Preparation--

A stainless steel tube as previously described previously was cleaned and packed atone end with glass wool to a depth of 2.5 cm. Cleaned Tenax was placed on top of the glass wool to a depth of approximately 25 cm. The top 2.5 cm of a tube was filled with glass wool to hold the Tenax in position. Both ends of a tube were capped with Swagelok fittings to complete the assembly of a sample cartridge. Approximately 600 cartridges were prepared and each was stamped with a unique serial number for identification.

The nuts on the compression fittings were tightened manually, then turned 1.25 revolutions further with a wrench.

An assembled sample cartridge is illustrated in Figure A-1.

Special Handling Precautions--

The caps on the sample cartridges were maintained in place to prevent contamination of the Tenax. During sampling the nuts were stored in Ziploc plastic bags to decrease the possibility of contaminating the cap assembly with ambient benzene and other pollutants.

Because Tenax is thermally unstable, and will decompose into other compounds (including benzene), the cartridges were kept in cold storage after preparation. The cartridges were stored at a temperature of -18°C in freezers at the sites and at the analysis laboratory. During transport to and from the sites, the cartridges were placed in Trans Temp Cool Paks, insulated shipping carriers containing an eutectic mixture. Field operators supervised shipment to the sites to ensure quality handling. One-day service by Federal Express was used to carry the samples from the sites to the analysis laboratory. Shipments occurred only on Mondays through Thursdays, so that the time the samples were removed from the freezers was minimized. To prevent condensation of water vapor, each cartridge was permitted to equilibrate to room temperature for 8 hours.

Sample Collection Procedure

Three sampling systems were used, distinguished by the number of sample cartridges and the method of connecting the cartridges to the samplers. The systems, using either single, duplicate, or tandem samplers, are illustrated in Figures A-2 through A-4.

The majority of samples was obtained over a 24-hour period with the single-cartridge sampler. The duplicate-cartridge sampler, with the cartridges connected in parallel, provided quality control data for assessing the accuracy of the sampling data. The tandem cartridge sampler, with the two cartridges connected in series, verified that benzene breakthrough did not occur in the upstream cartridge.

Sampling occurred over a period of 10 consecutive days, and the daily time period was delayed two hours between samples to prepare and clean the equipment. Sampling occurred from 7 a.m. to 7 p.m. the first day, 9 a.m. to 9 p.m. the second day, and continued in a similar manner for the duration of sampling. The duplicate quality-control samples were obtained during the second, fifth, and eighth days from one site in each of the six cities that were sampled.

The following data were recorded with each day's sample:

1. Location - city name and site number
2. Time - date sampling started and ended, time of day sampling started and ended, elapsed time from timer
3. Meteorology - temperature (daily maximum and minimum), relative humidity, barometric pressure, sky conditions (cloudy, clear, scattered showers, heavy rain, snow, smog), wind (calm, steady, gusty)
4. Type sampler - single, duplicate, tandem
5. Serial number of each sample cartridge
6. Flow rates - three measurements were obtained at each of three times - beginning, middle, and end of sampling (A total of nine measurements was obtained for each cartridge. The average flow rates determined for the three times were averaged to determine the average sample flow rate.)
7. Total volume sampled - product of average sample flow rate and elapsed time
8. Pump operating vacuum

Typical data recorded once for each site included:

1. Site location - building name, street address, city and state, general location (central business district, central core, outer core, old residential, inner suburb, outer suburb, rural)
2. Operating agency - name, street address, city and state, phone number, name of operator
3. Date - start and stop dates of sampling
4. Probe location - distance from curb, height above ground level, compass direction of exposure, distance below top of building (if applicable)
5. Street type - freeway, highway, commercial, or residential street, and number of lanes in each direction
6. Traffic condition - very heavy, heavy, medium, light, very light
7. Sampler data - manufacturer, model and serial numbers, type of pollutant monitored, and probe size and type of material.

Analytical Procedure

A sample was recovered by desorbing the benzene from the Tenax resin, liquifying it in a cryogenic trap, and separating it from miscellaneous organic compounds with a capillary column from which it was subsequently analyzed. Figure A-5 illustrates the sample flow during recovery and analysis.

A sample cartridge was removed from the storage freezer and placed in the desorption heater (presented in Figure A-6). Quick-connect fasteners enabled prompt fastening of the cartridge to valve ports (No. 3 and 4 of the four-port valve) with the 400-W heater being preheated to a temperature of 250°C. With the two valves positioned as indicated for sample recovery, helium carrier gas was permitted to flow at 30 cm^3/min through the cartridge and into the trap containing 60/80 mesh silanized glass beads, where benzene and other inorganic impurities were condensed. The sample was collected for 4 minutes. Also during this time the MBMA column was purged with helium at a flow rate of 6 cm^3/min. Immediately following recovery, the liquid nitrogen surrounding the trap was removed and replaced by an oil bath at a temperature of 190°C, which flash vaporized the benzene. After the trap had been in the bath for 1 minute, the two valves were positioned as indicated in the sample-analysis view (Figure A-5). The 6 cm^3/min flow of both helium and heat from the oil bath caused benzene gas to flow from the MBMA column 8 minutes after the valves were repositioned.

The benzene concentration was detected, measured, and recorded with a FID, GC, a data acquisition system, and strip chart recorder.

The operating conditions of the various components and reagents are summarized as follows:

Helium carrier gas - 6 cm^3/min, 50 psig
Air - catalytically cleaned, 450 cm^3/min, 50 psig
Hydrogen - 54 cm^3/min, 20 psig
Temperatures: Oven - 70°C for 8 min, followed by 120°C
Detector - 200°C
Valves - 150°C
Transfer lines - 150°C
Oil bath - 190°C
Desorption chamber - 250°C
Liquid nitrogen - (-200°C)

CALIBRATION AND STANDARDS

Calibration mixtures were purchased from Scott Environmental Research and used as working standards. The cylinder concentrations were verified by preparing a series of benzene gas standards in gravimetrically calibrated glass bulbs. These standards were injected into a gravimetrically calibrated gas sampling loop (1.1 ml). The glass bulb standard results showed that the Scott working standards were well within experimental error. Some of the tanks were also analyzed by other laboratories and the reported concentrations reported well within experimental error (better than 10%).

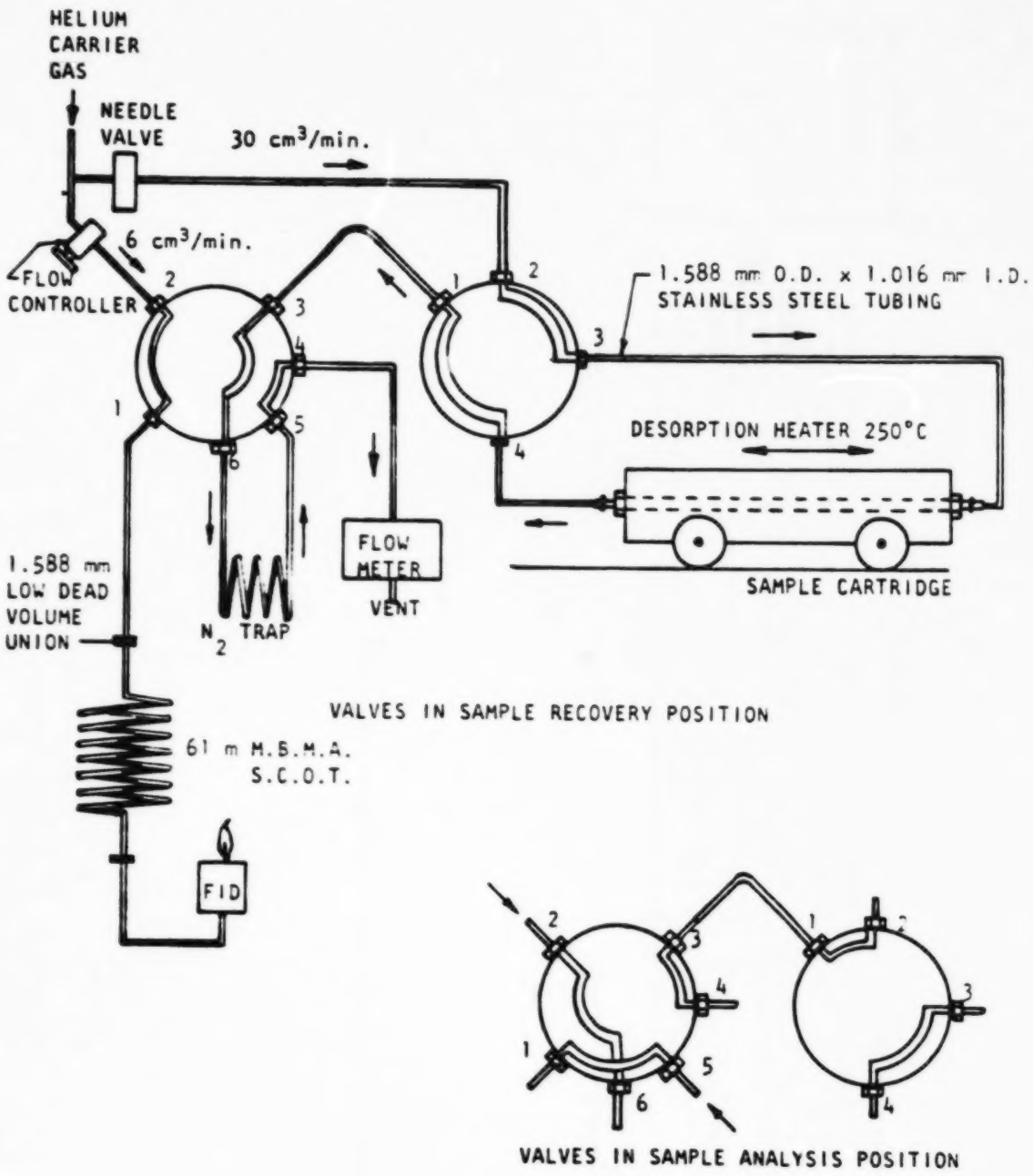

Figure A-5. Apparatus for sample recovery and analysis.

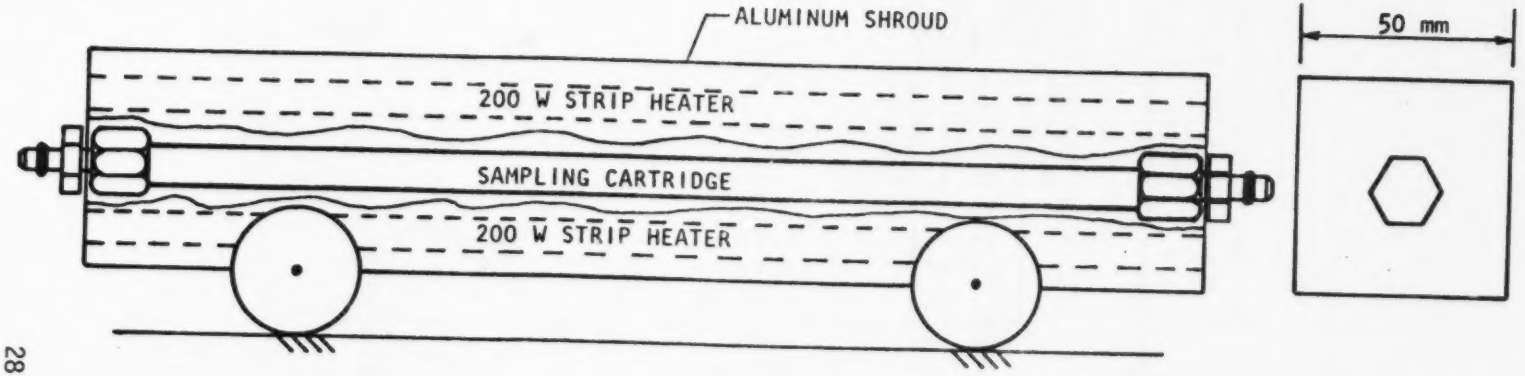

Figure A-6. 400-W modified desorption heater.

The detector response was checked by diluting portions of a 350 ppm tank to 2, 5, 41, and 200 ppm. A calibration curve was plotted using the results of these analyses; moreover, purchased mixtures of 13 and 72 ppm also were used to check the calibration curve.

The stability of working standards was inferred by studies of a 9.37 ppm calibration standard that was analyzed 36 times over a 2-month period. Maximum and minimum concentrations from the mean value were 20.5 and 9.7 percent, respectively, and the standard deviation was 8.7 percent. To obtain analyses accurate within 10 percent, a daily calibration was required.

CALCULATIONS

The volume of the air sample was not corrected to S.T.P. because of uncertainty in the 24-hour average temperature and pressure values. The air sample volume used in the analysis was determined as follows:

$$V_m = \frac{F_1 + F_2 + F_3}{3} \times T \times 10^{-6} \qquad \text{(A-1)}$$

where V_m = volume of gas sampled (uncorrected), m

F_1 = measured flow rate before sampling, cm^3/min

F_2 = measured flow rate after sampling, cm^3/min

F_3 = measured flow rate during sampling, cm^3/min

T = sampling time, min

The GC and data acquisition system were calibrated in units of ppm, which may be converted (Federal Register, 1971) to units of $\mu g/m^3$ as follows:

$$\mu g/m^3 = \frac{\text{molecular weight} \times 10^6}{24{,}470} \text{ (ppm)} \qquad \text{(A-2)}$$

$$= \frac{(78.1)\ 10^6}{24{,}470} \text{ (ppm)}$$

$$= 3192 \text{ (ppm)}$$

where the molecular weight of benzene is 78.1 g/mole and air is dry at 25°C and 760 mm Hg.

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1. Federal Register, 1971. 35:8186-8201.

2. Lodge, J. P., J. B. Pate, B. E. Ammons, and G. A. Swanson. The Use of Hypodermic Needles as Critical Orifice in Air Sampling. J. Air Pol Control A, 16(4):197-200, 1966.

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